

### **REMARKS**

Claims 1, 4-7, 10-16, 18, 21-23, 26, 27, 29, 30, and 32-34 are pending in the application and are at issue.

Claims 14-16, 18, 23, 26, 27, 29, 30, and 32-34 have been amended to recite that the crosslinked hydrogel is a particle. Support for these amendments can be found in the specification, for example, at page 3, lines 16-18; page 32, lines 6-13; and page 50, line 34 through page 51, line 10, for example.

Claim 21 has been amended to recite that the composition contains 0.1% to 5%, by weight, of the triacrylate ester; 0.5%-99.9% of at least one hydrophilic monomer M comprising (meth)acrylic acid, and a diluent G. Support for these amendments to claim 21 can be found in the specification at page 24, lines 27-34; page 25, line 4; original claim 22; and page 25, line 32 through page 26, line 23 (wherein monomer M includes (meth)acrylic acid).

The amendments to the claims clarify that the claimed esters are used as internal crosslinkers for (meth)acrylic acid to form hydrogel particles. These internally crosslinked hydrogel particles can be subjected to a second separate postcrosslinking step, wherein the crosslink density only in the vicinity of the particle surfaces is increased.

Claims 1 and 4-6 stand rejected under 35 U.S.C. §103 as being obvious over EP 0 777 287 (EP '287) based on a contention that EP '287 discloses an ester F wherein m and n values (discussed below) are explicitly taught to be low. Applicants traverse this rejection.

A determination that a claimed invention would have been obvious under §103(a) is a legal conclusion involving four factual inquiries: (1) the scope and content of the prior art; (2) the differences between the claimed invention and the prior art; (3) the level of ordinary skill in the pertinent art; and (4) secondary considerations, if any, of non-obviousness. *Graham v. John Deere Co.*, 383 U.S. 1, 17-18 (1966). Secondary considerations of non-obviousness include factors such as commercial success, long-felt but unresolved needs, the failure of

others, and/or *unexpected results achieved by the claimed invention*. *Id.* Obviousness is determined from the vantage point of a hypothetical person having ordinary skill in the art which the claimed subject matter pertains, who is presumed to have all prior art references in the field of the invention available to him/her. In *re Rouffet*, 149 F.3d 1350, 1357 (Fed. Cir. 1998). Furthermore, obviousness must be determined as of the time the invention was made and in view of the state of the art that existed at that time. *Uniroyal Inc. v. Rudkin-Wiley Corp.*, 837 F.2d 1044, 1050-51 (Fed. Cir. 1988).

The Patent Office must clearly articulate facts and reasons why the claimed invention "as a whole" would have been obvious to a hypothetical person having ordinary skill in the art at least as of the claimed invention's effective filing date. *KSR Int'l Co. v. Teleflex Inc.*, 127 S.Ct. 1727, 1741 (2007) (citing with approval In *re Kahn*, 441 F.3d 977, 988 (Fed. Cir. 2006) ("[R]ejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness.")).' see also MPEP §2143 ("The key to supporting any rejection under 35 U.S.C. §103 is the clear articulation of reason(s) why the claimed invention would have been obvious.").

To reach a proper determination under 35 U.S.C. §103(a), the examiner must step backward in time and into the shoes worn by the hypothetical "person of ordinary skill in the art" when the invention was unknown and just before it was made. In view of all factual information, the examiner must then make a determination whether the claimed invention "as a whole" would have been obvious at that time to that person. Knowledge of applicants' disclosure must be put aside in reaching this determination, yet kept in mind in order to determine the "differences," conduct the search, and evaluate the "subject matter as a whole" of the invention. The tendency to resort to "hindsight" based upon applicants' disclosure is often difficult to avoid due to the very nature of the examination process. However, impermissible hindsight must be avoided and the legal conclusion must be reached on the basis of the *facts* gleaned from the prior art. MPEP §2142.

Furthermore, to establish a *prima facie* case of obviousness, the examiner must satisfy three requirements. First, as the U.S. Supreme Court very recently held in *KSR International Co. v. Teleflex Inc. et al.*, 127 S.Ct. 1727 (2007), "a court must ask whether the

improvement is more than the predictable use of prior art elements according to their established functions. ...it [may] be necessary for a court to look to interrelated teachings of multiple patents; the effects of demands known to the design community or present in the marketplace; and the background knowledge possessed by a person having ordinary skill in the art, all in order to determine whether there was *an apparent reason* to combine the known elements in the fashion claimed by the patent at issue. ...it can be important to *identify a reason that would have prompted a person of ordinary skill in the relevant field to combine the elements* in the way the claimed new invention does... because inventions in most, if not all, instances rely upon building blocks long since uncovered, and claimed discoveries almost of necessity will be combinations of what, in some sense, is already known." (emphasis added, *KSR, supra*). Second, the proposed modification of the prior art must have had a reasonable expectation of success, determined from the vantage point of the skilled artisan at the time the invention was made. *Amgen Inc. v. Chugai Pharm. Co.*, 18 USPQ2d 1016, 1023 (Fed. Cir. 1991). Lastly, the prior art references must teach or suggest all the limitations of the claims. *In re Wilson*, 165 USPQ 494, 496 (C.C.P.A. 1970).

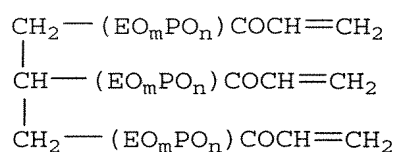
As recently articulated by the Court of Appeals for the Federal Circuit in *Ortho-McNeil Pharmaceutical Inc. v. Mylan Laboratories Inc.*, 86 USPQ 2d, 1196, 1201-2 (Fed. Cir. 2008):

"As this court has explained, however, a flexible TSM test remains the primary guarantee against a non-statutory hindsight analysis such as occurred in this case. *In re Translogic Tech., Inc.* 504 F.3d 1249, 1257 [84 USPQ 2d 1929] (Fed. Cir. 2007) ("[A]s the Supreme Court suggests, a flexible approach to the TSM test prevents hindsight and focuses on evidence before the time of invention.)."

Once the Patent Office properly sets forth a prima facie case of obviousness, the burden shifts to the applicants to come forward with evidence and/or argument supporting patentability. *See In re Glaug*, 283 F.3d 1335, 1338 (Fed. Cir. 2002). Rebuttal evidence is merely a showing of facts supporting the opposite conclusion." *In re Piasecki*, 745 F.2d 1468, 1472 (Fed. Cir. 1984). Evidence rebutting a prima facie case of obviousness can include: (a) "evidence of unexpected results," *Pfizer, Inc. v. Apotex, Inc.*, 480 F.3d 1348 1369 (Fed. Cir. 2007); (b) "evidence that the prior art teaches away from the claimed invention in

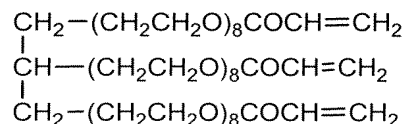
any material respect," *In re Peterson*, 315 F.3d 1325, 1331 (Fed. Cir. 2003); and, (c) evidence of secondary considerations, such as commercial success or long-felt yet unmet needs, *WMS Gaming, Inc. v. International Game Tech.*, 184 F.3d 1339, 1359 (Fed. Cir. 1999). The Patent Office must always consider such evidence supporting patentability. *See, e.g., In re Sullivan*, 498 F.3d 1345, 1352-53 (Fed. Cir. 2007) (reversing a Patent Office decision of obviousness because the Patent Office failed to consider the applicants' evidence rebutting a prima facie case of obviousness because the Patent Office failed to consider the applicants' evidence rebutting a prima facie case of obviousness). If the Patent Office determines that such evidence is not compelling or is insufficient, then the Patent Office should specifically set forth the facts and reasoning supporting that determination. MPEP §2145 (8<sup>th</sup> Ed., Rev. 6, Sept. 2007).

The EP '287 rejection is based on formula (2), i.e., the *sole* glycerol-based compound of EP '287, having a formula:



wherein m and n do not represent 0 at the same time and  $0 \leq n$  and  $0 \leq m$  (EP '287, page 4, line 32). Accordingly, either EO *or* PO can be absent from the compound, and *no* "upper limit" exists for m, n, or the sum of m+n. EP '287 therefore discloses an infinite number of compounds.

In the examples of EP '287, the sole example directed to a glycerol-based compound is Embodiment 4, wherein n=8 and m=0, i.e., compound (7) at page 8 of EP '287, illustrated below. This compound is (a) free of PO units and (b) contains a sum of 24 EO units.



It further must be noted that EP '287 is directed to non-aqueous electrolyte batteries having a negative electrode coated with a polymer film prepared from the compounds disclosed in EP '287. The EP '287 reference fails to teach how to prepare the disclosed compounds, fails to teach copolymerization of the disclosed compounds, fails to suggest the use of compounds as a crosslinker for monoethylenically unsaturated monomers, and is in no way related to superabsorbent polymers (SAPs) and a reduction of residual monomers in the production of SAPs.

For the reasons set forth herein, it is submitted that EP '287 fails to render present claims 1 and 4-6 obvious under 35 U.S.C. §103.

Present claims 1 and 4-6 are directed to an ester F wherein the *total* number of EO and PO units in a claimed ester F (not in each alkylene oxide chain) is 3, 4, or 5, as recited.

The general teachings of EP '287 are to a broad a range of compounds, including both glycerol-based compounds and trimethylolpropane-based compounds. EP '287 discloses an infinite number of compounds because no upper limit is placed on either variable "m" or "n". In addition, either "m" or "n", but not both, can be zero.

The *sole* specific example of EP '287 directed to glycerol-based compounds is compound (7) which contains 24 EO groups and no PO groups. Accordingly, EP '287 fails to disclose any specific examples within the claimed range, i.e., a glycerol-based compound containing EO and PO groups, wherein the sum of EO and PO is in the claimed narrow range of 3 to 5. All examples in EP '287 contain from 6 to 48 total EO and/or PO units.

To further demonstrate that EP '287 fails to render claims 1 and 4-6 obvious under 35 U.S.C. §103, the presently claimed esters exhibit unexpected benefits in the preparation of superabsorbent polymers (SAPs).

In the present specification, Table 1 at page 51 includes seven esters (a through g) that are tested as crosslinkers in the preparation of an SAP. Examples f and g are comparative in that they (a) are based on trimethylolpropane (TMP), (b) contain only EO units, and (c) contain more than a total of 5 EO and PO groups, i.e., Example g. Examples a-

e are esters of the present claim 1, i.e., based on glycerol, contain EO or EO and PO units, and contain a total of up to 5 PO and EO units. Comparative Example g is similar to an example to the EP '287 disclosure, i.e., based on TMP, containing only EO units, and containing 15 EO units. See Embodiment 1 of EP '287, based on TMP and containing 18 EO units and no PO units. Comparative Example f also is based on TMP and contains 3 EO units, and is close to first entry in Table 1 of EP '287 based on TMP and containing 6 EO units. The only embodiment of EP '287 based on glycerol contains only EO and the total number of EO units is 24.

The data in Table 2 of the specification shows that claimed esters a-e provide an SAP having a very low crosslinker residue (over replicate tests) of from less than 5 to 10 ppm. In contrast, a crosslinker based on TMP and containing 15 EO units (i.e., g) provided in SAP having a 20 to 51 ppm crosslinker residue. A comparative crosslinker based on TMP and containing only 3 EO units (Example f) provided an SAP having 857 to 1302 ppm of residual crosslinkers.

In addition, the claimed esters a-e provided SAPs having a VSI value (saponification index) of 7.5 to 11.1. Comparative TMP-based esters f and g demonstrated a VSI value of 36.9 and 11.6, respectively.

The presently claimed esters therefore show unexpected results with respect to crosslinker residue, which ideally is zero to avoid free monomers in the resulting SAP or the need to perform a method step to remove the crosslinker residue. Unexpected results also are demonstrated with respect to VSI values. As stated in the specification, an ideal crosslinker has a VSI of zero because then all crosslinking is performed during the reaction, as opposed to during a drying step. In turn, the properties of the SAP are not altered by the drying process. See specification, page 50, lines 1-6.

In addition, the test data discussed above not only is unexpected, but shows the unpredictability in the art. In particular, changing glycerol to TMP results in crosslinking agents that vary considerably with respect to residual crosslinkers remaining after a polymerization. It is the presently claimed compounds, i.e., based on the glycerol, containing both EO and PO, and 3 to 5 total EO/PO moieties that provided the unexpected results.

These results could not have been predicted from the disclosure of EP '287, which equate glycol and TMP.

In view of the broad disclosure of EP '287, including (a) trimethylolpropane and glycerol-based triacrylates, (b) that the disclosed compounds can be free of either EO or PO units, (c) that the number of disclosed compounds is infinite (i.e.,  $m \leq 0$  and  $n \leq 0$ ), (d) that the examples are primarily directed to TMP-based compounds, and (e) that the only glycerol-based example contains 24 EO units only, *and* the unpredictability in the art, *and* the demonstrated unexpected results, it is submitted that EP '287 cannot render claims 1 and 4-6 obvious under 35 U.S.C. §103.

The present claims are closely tailored to be based on glycerol, and contain a total *sum* of EO and PO units of 3, 4, or 5, wherein the esters demonstrate unexpected results with respect to performing as a crosslinking agent for an SAP. EP '287 further is directed to homopolymers, and the disclosed esters are not used, or even considered, as crosslinking agents for (meth)acrylic acid. EP '287 also provides no direction, guidance, or apparent reason for a person skilled in the art of SAPs to select the narrow range of claimed compounds from the infinite number of compounds in the reference (which is directed to a non-aqueous electrolyte secondary battery) with any reasonable expectation of providing a crosslinker for SAPs having unexpectedly improved properties over SAPs crosslinked with other esters *also* disclosed in EP '287 and *closer* in structure than the compounds disclosed in EP '287.

The examiner relies upon Table 1 of EP '287 for teaching low values for "n", i.e., the number of ethylene oxide units *per* hydroxy group, and that the reference primarily focuses on low "n" values. First, the reference does not focus on compounds of low "n" value. The examiner is directed to Embodiments 1, 3, and 4 of EP '287 teaching "n" values of 6 and 8 (18 to 24 EO units) that *outperformed* the low "n" value compounds of Embodiment 2 by exhibiting longer life cycles.

The examiner also should realize from formula (7) of EP '287 disclosed that the disclosed compounds contain 3 "n"'s, and therefore, the lowest number of ethylene oxide units disclosed in EP '287, Table 1, is six. This is greater than the total number of EO/PO

units claimed, and all other entries in Table 1 of EP '287 contain *more* than 6 EO/PO units. Also, note that the compounds of Table 1 *exclude* propylene oxide units. Importantly, the compounds of Table 1 in EP '287 are based on formula (5) of EP '287. Formula (5) is *not* a glycerol-based compound as claimed, but is based on trimethylolpropane. Further, Table 1 shows a *shorter* cycle life for compounds having 6 total EO units (n=2) compared to compounds having 12 total EO units (n=4), compounds having 18 total EO units (n=6), and compounds having 24 total EO units (n=8). Table 2 of EP '287, as discussed above, also exhibit better life cycles than compounds having low "n" values.

Persons skilled in the art therefore are discouraged by EP '287 from using a low total number of alkylene oxide units. In contrast to the compounds in Table 1, a presently claimed ester is based on glycerol and cannot contain six ethylene oxide units. The maximum number of ethylene oxide units in the claimed esters is 1 to 4, *and* propylene oxide units can be present. EP '287 fails to provide any guidance or suggestion that would lead a person skilled in the art to a presently claimed ester with any reasonable expectation of providing a crosslinker that provides an SAP having improved properties, especially over compounds that are close in structure to claimed ester F and also broadly disclosed in EP '287.

For all of the reasons set forth above, it is submitted that claims 1 and 4-6 would not have been obvious to a person skilled in the art under 35 U.S.C. §103.

Claims 7, 10-18, and 21-23 stand rejected under 35 U.S.C. §103 as being obvious over EP '287 in view of Barthold et al. U.S. Patent No. 5,472,617 ('617). Applicants traverse this rejection. Claim 17 was previously cancelled from the application.

EP '287 and the patentability of compound claims 1 and 4-6 over EP '287 has been discussed above. Claims 7, 10-18, and 21-23 are directed to (a) methods of preparing the esters of claim 1 (claims 7 and 10-13), (b) to methods of preparing a crosslinked hydrogel using an ester of claim 1 (claims 14-16), (c) to a crosslinked hydrogel comprising an ester of claim 1 (claim 18), and (d) a composition containing an ester of claim 1 and a hydrogel prepared from the composition (claims 21-23). EP '287 absolutely (a) fails to teach how to prepare the esters disclosed therein, as recited in claims 7 and 10-13, (b) fails to teach a



method of preparing a hydrogel or a hydrogel containing the disclosed esters, as recited in claim 14-16 and 18, and (c) fails to teach a composition and hydrogel prepared therefrom as recited in claims 21-23.

The '617 patent fails to overcome these deficiencies of EP '287. The '617 patent is directed to a method of demulsifying a crude oil and water mixture using copolymers of (meth)acrylic acid and hydrophilic comonomers. The copolymers are prepared by copolymerizing a (meth)acrylate of an alkoxyated alcohol, diol, or triol with a comonomer, e.g., acrylic acid. The '617 patent generally teaches monofunctional and multifunctional alcohols at column 3, lines 36-53. Glycerol is disclosed among more than specific 20 alcohols. The '617 patent also discloses 15 alkoxyated alcohols at Table 1 of the reference. No disclosed alkoxyated alcohol in the examples is glycerol, and the ratio of alcohol to alkylene oxide is far above the ratio of 1 to 3 and 1 to 4 recited in claims 18 and 21, e.g., Example a3 of the '617 patent has a ratio of 1 to about 49, Example a4 has a ratio of 1 to about 36, Example a5 has a ratio of 1 to about 66, and Example a6 is 1 to about 40.

The specific teachings of the '617 patent therefore are directed to alkoxyated alcohols containing a high amount of alkylene oxide in order to perform their intended function of demulsifying a crude oil emulsion. Persons skilled in the art, after reading the '617 patent, would have had no apparent reason to select glycerol from the long list of disclosed alcohols, then alkoxyate with only 3 or 4 ethylene oxide and/or propylene oxide units. In addition, the copolymers of the '617 patent contain a *major* amount of a (meth)acrylate of an alkoxyated alcohol/polymer and a minor amount of hydrophilic comonomer. See Table 4 showing a major amount of Ester 1 copolymerized with a minor amount of first comonomers (e.g., acrylic acid). This is the exact opposite of the relative amounts of monomers present in a claimed hydrogel particle.

The '617 process of preparing an alkoxyated (meth)acrylic ester is disclosed in the Examples, which the examiner relies upon to support the obviousness rejection. See '617 patent, column 8, line 65 through column 11, line 6. In this process, an alkoxyated trimethylolpropane (TMP) is mixed with acrylic acid *under a nitrogen atmosphere* and the reaction is allowed to proceed to yield an acrylic ester of alkoxyated TMP (column 10, line 52 through column 11, line 6, wherein 268 g of xylene are used as a solvent *and* 268 g of the

xylene *remained* after the reaction, see in particular column 10, lines 54 and 55 and columns 11 and 12, Table 3, A14). The nitrogen atmosphere is applied prior to and maintained during the reaction. After the reaction is complete, the '617 patent teaches that the mixture is cooled, then reacted with acetic anhydride (column 11, lines 2-5), with *no* loss of solvent, as discussed above, i.e., the solvent was not stripped from the reaction mixture.

The '617 patent also discloses that one equivalent of (meth)acrylic acid is used per equivalent of hydroxyl groups in the alkoxyated alcohol. Specifically, the '617 patent, at column 4, line 63 through column 5, line 1 states:

"The ratio of the oxyalkylated alcohol to acrylic acid or methacrylic acid may be varied from 1:1 to 1:n, where n is the functionality (i.e. the number of hydroxyl groups) of the starting alcohol. A ratio of 1:1 is preferred, since otherwise gelling may be observed during the subsequent polymerization."

The '617 patent therefore discourages, and actually teaches away, from using an excess amount of (meth)acrylic acid in the reaction with the alkoxyated alcohol. In particular, the '617 patent teaches a preference for a deficit of (meth)acrylic acid to alcohol by teaching a 1:1 ratio even when n is *greater* than one, for example, when n=3 as with glycerol.

The examiner bases the obviousness rejection on an assertion that the '617 patent purportedly discloses stripping with a gas which is inert under the reaction conditions. This assertion is incorrect.

First, the examiner is reminded that the references must render the invention obvious *as a whole* in order to support a rejection under 35 U.S.C. §103. In this regard, note that claim 7 recites a process for preparing an ester F in the presence of a molar excess of (meth)acrylic acid to alkoxyated glycol of at least 3.15:1, and at least 15:1 in claim 13. In contrast, the '617 patent specifically teaches that a molar excess of (meth)acrylic acid should be *avoided* and that a molar *deficit* is preferred. See '617 patent, column 4, line 63 through column 5, line 1. The examiner has completely ignored the claimed feature of excess (meth)acrylic acid, and as a result has failed to consider the invention as a whole. Also see claim 10, wherein no more than 75% of the excess (meth)acrylic acid is removed from the reaction mixture; claim 12, wherein at least 0.5%, by weight, (meth)acrylic acid remains in

the reaction mixture; and claim 13, which recites a molar excess of (meth)acrylic acid to alkoxyated glycol of at least 15:1.

Another major difference between claim 7 and the '617 patent is that "stripping" is different from a "nitrogen blanket". Applicants previously provided the examiner with *Hawley's Condensed Chemical Dictionary, Thirteen Ed.* (1997), page 1052, containing a definition of "stripping" showing that the term refers to the *removal* of volatile components from a liquid mixture by the passage of a gas through the liquid mixture. This stripping removes a solvent from the reaction mixture *after* the polymerization.

With further respect to the claimed feature of stripping with a gas, at column 10, line 52 through column 11, line 2, the '617 patent discloses *reacting* an alkoxyated alcohol with acrylic acid "under a nitrogen blanket". This is not equivalent to the stripping step i) recited in claim 7. Note that the nitrogen blanket in the '617 patent is applied *during* the reaction between the alkoxyated alcohol and the acrylic acid. The disclosed "nitrogen blanket" is not performing a stripping function, but, as well known in the art, is applied over a reaction mixture in the '617 patent to *preclude* the introduction of oxygen into the reaction system.

The presently claimed stripping step i) is performed *after* the reaction between the alkoxyated glycol and the (meth)acrylic acid to form the ester F. For example, the presently claimed stripping step i) is performed *after* the reaction between the alkoxyated glycol and the (meth)acrylic acid to form the ester F. See specification, page 22, lines 14-20, disclosing a "solvent stripping operation i)". Also see specification, page 21, line 24 through page 22, line 12, further disclosing the solvent removal steps. In contrast, the '617 patent teaches a nitrogen atmosphere over a reaction between an alkoxyated trimethylolpropane (Example a5) and acrylic acid ('617 patent, column 10, lines 41-55). Further, as stated above, the amount of xylene present at the beginning of the reaction and after completion of the reaction is the same, thereby showing that the nitrogen blanket does not perform a stripping function as asserted by the examiner.

Further, the '617 patent teaches that "a *solution* of the essential alcohol" from a previous example is used in subsequent polymerization reactions (e.g., column 14, lines 62-63), further showing that solvent was not stripped in the '617 patent disclosure.

Another major difference between the '617 patent and claim 7 is that the stripping is performed using an "oxygen-containing gas", as presently recited in amended claim 7. The teachings of the '617 patent are limited to nitrogen gas. An oxygen-containing gas is utilized in the stripping step to maintain the inhibitory capabilities of a compound like MEHQ during solvent removal, i.e., to inhibit premature polymerization of the formed ester F. It is well-known in the art that oxygen must be present to maintain this polymerization inhibitory capability. Applicants also previously submitted to the examiner, an excerpt from "Modern Superabsorbent Polymer Technology" (1998), pages 39-44, showing the influence of oxygen on polymerization inhibition.

The '617 patent utilizes a nitrogen blanket to *remove* oxygen from the reaction system and *keep* oxygen out of the system, such that the inhibition capabilities of MEHQ are reduced and the polymerization can proceed. This is exactly the opposite of the present invention, wherein the inhibiting capabilities of an inhibitor like MEHQ are maintained. The disclosed "nitrogen blanket" is not a stripping function, but as is well known in the art, is applied over a reaction mixture in the '617 patent to preclude the introduction of oxygen into the reaction system. Accordingly, the "nitrogen blanket" of the '617 patent and the "stripping" step are not identical (e.g., are performed at different steps of the reaction and perform different functions).

Further, the '617 patent fails to teach or suggest a mole excess of at least 3:15:1 of (meth)acrylic acid in the reaction mixture. The '617 patent fails to consider or address using such mole excess of (meth)acrylic acid, and provides no apparent reason for a person skilled in the art to use such a molar excess of (meth)acrylic acid. In contrast, the '617 patent, at column 4, line 63 through column 5, line 1, specifically teaches a maximum of a 1:n molar ratio (per hydroxyl group of the alcohol) of oxyalkylated alcohol to (meth)acrylic acid, and a preferred 1:1 ratio regardless of the number of hydroxyl groups, and therefore an excess of (meth)acrylic acid *should be avoided*.

With respect to claim 10, the '617 patent teaches that a preferred 1:1 molar ratio of oxyalkylated alcohol to (meth)acrylic acid should be used, and that no more than a 1:n ratio should be used, wherein "n" is the number of hydroxyl groups of the alcohol/polyol. Therefore, the resulting reaction product cannot contain an excess amount (meth)acrylic acid. The '617 patent actually teaches a preferred 1:1 ratio, regardless of the "n" value, and, accordingly a preferred deficit of (meth)acrylic acid. In addition, a step of removing no more than 75% by weight of excess (meth)acrylic acid is neither taught nor suggested in the '617 patent, and cannot be taught because no excess (meth)acrylic acid is present in the reaction mixture.

The '617 patent fails to teach every feature of claims 7 and 10-13, and, in fact, fails to teach more than one feature of claim 7. Claims 7 and 10-13, therefore, would not have been obvious under 35 U.S.C. §103 over the '617 patent. The '617 patent fails to teach or suggest a solvent stripping step, or using an excess molar amount of (meth)acrylic acid, let alone both claimed features, *and* fails to provide any apparent reason for performing such steps.

The examiner also has failed to articulate clear reasons, with support, why the presently claimed invention, as a whole, would have been obvious over the '617 patent. Numerous jumps in reasoning would have been required to arrive at the present invention after reading the '617 patent, one of which is expressly taught as being avoided by the '617 patent. The '617 patent therefore does not provide an incentive or apparent reason for a person skilled in the art to modify the '617 patent in a manner needed to arrive at the presently claimed invention. In summary, process claims 7 and 10 are patentable over the cited '617 patent, and the rejection should be withdrawn.

With further respect to claims 11-13, the examiner has totally failed to articulate reasons why claims 11-13 would have been obvious over the '617 patent, except for a conclusory statement relating to "routine experimentation". In particular, at page 9 of the Office Action, the examiner states:

"Nevertheless, Barthold et al. (col. 8, line 65 to col. 9, line 40; col. 9, Table 1; col. 11, Table 3) have clearly disclosed a process for preparing the compound ester F as claimed. Therefore, the examiner believes that it would

have been obvious to one of ordinary skill in art to use "routine experimentation" technique to optimize the process of Barthold et al. to obtain the invention of claims 11-13. In re Aller, 220 F.2d 454, 456, 105 USPQ 233, 235 (CCPA 1955)."

The examiner is directed to the *KSR Int'l Co. v. Teleflex*. The mandate of the United State Supreme Court is that the Patent Office *must* make it clear in the record with *facts* and *reasoning* that the teaching-suggestion-motivation to modify the reference exists. As emphasized by the Supreme Court, "rejections on obviousness grounds cannot be sustained by mere conclusory statements; instead, there must be some articulated reasoning with some rational underpinning to support the legal conclusion of obviousness." *KSR Int'l Co.* 127 S.Ct 1741. See also MPEP §2143 ("The key to supporting any rejection under 35 USC § 103 is the clear articulation of reason(s) why the claimed invention would have been obvious."), and *Ortho-McNeil Pharmaceutical* 86 USPQ at 1201-2 ("a flexible TSM test *remains* the primary guarantee against a non-statutory hindsight analysis (emphasis added).).

It is submitted, therefore, that the present rejection does not provide any articulated reasoning to support a conclusion of obviousness of claims 11-13 over the '617 patent, and that this rejection should be withdrawn.

In addition, claim 13 recites a molar ratio of (meth)acrylic acid to alkoxylated glycerol in step a) of *at least 15:1*. The '617 patent absolutely fails to teach, suggest, or even consider such a mole excess of (meth)acrylic acid in the reaction mixture, as stated above. In contrast, the '617 patent, at column 4, line 63 through column 5, line 1 specifically teaches that a molar excess of (meth)acrylic acid *should be* avoided and that a molar deficit is preferred. This alone demonstrates the nonobviousness of claim 13 over the '617 patent, and provides an additional reason why the rejection should be withdrawn.

Claims 14-16 are directed to a method of preparing crosslinked hydrogel particles. Neither EP '287 nor the '617 patent teach or suggest the preparation of a hydrogel or of particles. In addition, claim 16 depends from claim 7, and is patentable for the reasons set forth above with respect to the rejection of claim 7 over a combination of EP '287 and the '617 patent.

With respect to claims 14 and 15, each claim recites a postcrosslinking step and a drying step in the preparation of particles. EP '287 and the '617 patent fail to disclose either of these steps, let alone both. The examiner again is reminded that a reference must teach or suggest *all* claimed features in order to establish a *prima facie* case of obviousness. Accordingly, because the references, alone or in combination, do not teach each limitation of claims 14-16, a *prima facie* obviousness rejection of the claims under 35 U.S.C. §103 cannot be maintained over EP '287 and the '617 patent.

In particular, the '617 patent fails to teach a postcrosslinking step or a drying step to prepare particles, and provides no apparent reason for a person skilled in the art to perform such steps. It must be noted that an SAP particle is postcrosslinked to improve fluid absorption properties. The polymers of the '617 patent are not SAPs, but rather are oil demulsifiers. Thus, an improvement of fluid absorption properties is neither considered nor addressed by the '617 patent. In summary, claims 14-16 are patentable over a combination of EP '287 and the '617 patent.

Claims 18 and 21-23 are directed to a crosslinked hydrogel particle and a composition for preparing a crosslinked hydrogel particle. The patentable differences between claim 21 relating to ester F of claim 1 and the EP '287 patent has been discussed above. In addition, contrary to the '617 patent, the composition includes a *minor* amount of ester F and a *major* amount of a hydrophilic monomer comprising (meth)acrylic acid. The ester F is present in an amount sufficient to internally crosslink the hydrophilic monomer and provide a crosslinked hydrogel particle (claim 23). Note that surface postcrosslinking (claim 23) is *independent* of internal crosslinking.

EP '287 is not remotely directed to crosslinked hydrogels. The compounds disclosed in EP '287 are homopolymerized. The '617 patent does not overcome this deficiency.

With respect to ester F of claim 18, the '617 patent specifically discloses a ratio of alcohol to alkoxides of from 1:120 to 1:5. See '617 patent at column 3, lines 64 and 65. Stated alternatively, the '617 patent recites a sum 5 to 120. In contrast, claims 18 and 21 recite a sum of  $p_1 + p_2 + p_3$  is 3 or 4. See page 18, above, for a discussion of the '617 patent.

Persons skilled in the art, after reading the '617 patent, would have had no apparent reason to select glycerol from the long list of disclosed alcohols, then alkoxylate with only 3 or 4 ethylene oxide and/or propylene oxide units with any reasonable expectation that the resulting compounds could serve as a crosslinker for an SAP that demonstrates unexpected benefits with respect to reducing the amount of residual monomers (see examples). Further, as stated above, the '617 patent teaches polymers containing a *major* amount of the alkoxylated triacrylates and a *minor* amount of (meth)acrylic acid. This is the exact opposite of the crosslinked hydrogel particles of the present invention, and the ratios used in the '617 patent would be too greatly crosslinked to perform as an SAP. Accordingly, it is submitted that claims 18 and 21-23 would not have been obvious to a person of ordinary skill in the art over EP '287 in view of the '617 patent.

With respect to the examiner's contentions regarding the '617 patent and the term "diluent" in claim 22, claim 10 of the '617 patent refers to an oil/water mixture to which the copolymer is added to *effect* demulsification. The "crude oil and water mixture" is *not* present in the composition prior to polymerization as recited in claim 21, but is present after polymerization. See '617 patent, column 8, lines 40-61. Contrary to a statement in the Office Action, the examiner's reasoning has *no* basis. Claim 22 previously was clarified to recite that the diluent is water and/or a water-soluble organic solvent.

With respect to the examiner's comments regarding the '617 patent at column 1, lines 52-62, this portion of the '617 specification is directed to *prior* resins that demonstrates *disadvantages*, such as gelling. The '617 patent disclosure is not directed to the resins disclosed at column 1, lines 52-62, but to resins that may *overcome* these disadvantages. The '617 patent therefore is directed to resins that do *not* gel, in contrast to the presently claimed SAPs.

In summary, it is submitted that a case of *prima facie* obviousness of claims 7, 10-16, and 21-23 over EP '287 in view of the '617 patent has not been established and should be withdrawn.

Claims 26, 27, 29, 30, and 32-34 stand rejected under 35 U.S.C. §103 as being obvious over EP '287 in view of the '617 patent. Applicants traverse this rejection.



First, claims 26, 27, 29, 30, and 32-34 each depend directly or indirectly from claim 14, which is directed to a process for preparing hydrogel particles comprising a claimed ester F and (meth)acrylic acid. EP '287 fails to teach a copolymer or a hydrogel as recited in the present claims, but recites a highly crosslinked homopolymer of the compounds disclosed therein. See EP '287, Examples and page 4, lines 34-42. EP '287 fails to teach any hydrophilic comonomer and the highly crosslinked polymers of EP '287 are not hydrogels or particles. Therefore, the examiners contention that the polymer of EP '287 and the claimed crosslinked hydrogels are substantially identical is incorrect.

With respect to claims 26, 27, 29, 30, and 32-34, EP '287 and the '617 patent are silent with respect to the features recited in any of these claims. The references fail to disclose crosslinked hydrogel particles having a saponification index of less than 11 (claim 26), less than 8 (claim 32), or less than 5 (claim 33). The references also fail to disclose a crosslinked hydrogel particle having a reduced crosslinker content of less than 10 ppm (claim 27) or less than 5 ppm (claim 34).

With respect to article claims 29 and 30, the references are silent with respect to including a disclosed polymer in any article, but merely teach use of the polymer as a demulsifier and as an electrode coating.

In summary, it is submitted that claims 26, 27, 29, 30, and 32-34 are patentable over EP '287 in view of the '617 patent for the reasons set forth above and for the same reasons claims 7, 10-16, 18, and 21-23 are patentable over these references under 35 U.S.C. §103, and that this rejection should be withdrawn.

In the Office Action at pages 11-18, the examiner makes several statements in response to applicants' prior arguments in an attempt to support his rejections. These statements either are incorrect and/or strain credulity, even giving pending claims their broadest possible interpretation.

(a) the examiner's comments regarding a previous rejection under 35 U.S.C. §102(b) are irrelevant. No claim presently stands rejected under 35 U.S.C. §102(b).

(b) at page 12 of the Office Action, the examiner states:

"Applicants further argue that the claimed invention is not considered obvious in view of the unexpected results presented in the specification (page 51-52, Table 1 and 2). However, applicants must recognize that the comparative data are not commensurate to the scope of the claimed invention because the claimed invention is much broader than the scope encompassed by comparative data."

Applicants disagree. The claims are closely tailored to be based on glycerol, contain EO and/or PO units, and contain a total sum of EO and PO units of 3, 4, or 5. Therefore, the number of compounds recited in the claims is quite small. Tables 1 and 2 provide data for five of the claimed compounds (a-e), and comparative data for two compounds that are similar to the five claimed compounds differing only in containing TMP rather than glycerol or containing 15 EO units. Applicants data, as explained above, exhibits unexpected results over the closest prior art, i.e., tested compounds with the least and greatest claimed number of EO and PO units, i.e., three and five, which is closest to the compounds of EP '287. Also note that Table 1 of EP '287, relied upon by the examiner, contains 6 EO units on TMP.

(c) At page 13 of the Office Action, the examiner states:

"Regarding applicants' argument that the specification indicates that the oxygen containing gas contains a compound like MEHQ, the argument is not supported by the claims as written."

The statement is totally erroneous and shows a misunderstanding of the invention. The oxygen-containing gas is utilized in the stripping step to *maintain* the inhibition capabilities of a compound, like MEHQ, during solvent removal. This inhibits premature polymerization of the formed ester F. The MEHQ is *not* present in the oxygen-containing gas. The MEHQ is an inhibitor added to (meth)acrylic acid and is present via the addition of (meth)acrylic acid to glycerol in the formation of ester F. The MEHQ is still present when the ester F is formed and continues to act as an inhibitor to prevent premature reaction of ester F. The examiner's statement therefore is completely erroneous. The MEHQ is *not* present in the oxygen-containing gas and therefore cannot be claimed as such.

(d) at page 13, the examiner further states:

"Regarding applicants' argument that the blanketing with an oxygen containing gas of Barthold et al. does not equate to stripping, applicants fail to

recognize that blanking [sic] or stripping, both require an oxygen containing gas to be passed through the reactants, which can carries some of the reaction contents in the process. Therefore, the examiner has a reasonable basis to maintain that blanketing and stripping are functionally equivalent in the teachings of Barthold et al."

The examiner misunderstands the differences between "blanketing" and "stripping", which has been explained in prior responses and herein. A "blanketing" gas is passed *over* the reaction mixture, and typically is an inert gas to remove and prevent *oxygen* from adversely affecting the reaction. The blanketing gas of the '617 patent, e.g., nitrogen, does not contain oxygen, but is intended to purge oxygen from the system. The "stripping" gas is used to remove a solvent from a reaction mixture. It may be passed over the reaction mixture of bubbled through the reaction system. In the present invention, the stripping gas further *requires* the presence of oxygen in order to maintain the inhibiting capabilities of MEHQ, as discussed above. See the '617 patent, cited by the examiner, column 4, lines 61-63, disclosing the use and purpose of MEHQ, and that it is *not* in the stripping gas. The examiner's comment that both stripping or blanketing "require an oxygen containing gas" is incorrect. The '617 patent uses nitrogen, which does not contain oxygen.

(e) at page 13, the examiner further states:

"Regarding applicants' argument that Barthold et al. fail to teach the claimed molar excess of methacrylic acid to alkoxyated glycol of at least 3.15:1 because Barthold et al. (col. 4, line 63 to col. 5, line 1) only teach a molar ratio of 1:1, the examiner disagrees. Applicants fail to recognize that Barthold et al. (col. 5, line 13-16) clearly disclose the ratio as claimed. Applicants fail to recognize that Barthold et al. clearly teach the molar ratio of methacrylic acid to oxyalkylated alcohol to range from n:1 to 1:1, where n is the number of hydroxyl groups of the starting alcohol."

Again, the examiner shows a misunderstanding of the invention and of the '617 patent. The '617 patent teaches the alkoxylation of alcohols and polyols (Table 1). These alcohols and polyols contain one (nonylphenol), two (propylene glycol), three (trimethylolpropane), or six (sorbitol) hydroxyl groups, i.e., n is 1, 2, 3, or 6. The alkoxyated alcohols and polyols then are reacted with methacrylic acid (Table 3). As recognized by the examiner, the '617 patent teaches a molar ratio of (meth)acrylic to oxyalkylated alcohol to range from n:1 to 1:1, wherein n is the number of hydroxyl groups (otherwise gelling will occur). The '617 patent

teaches a preference for a 1:1 molar ratio, or a molar *deficit* of (meth)acrylic acid, when  $n > 1$ . Therefore, Barthold clearly discloses that an excess of (meth)acrylic acid should not be used. This is in contrast to the claims that recite at least a 3.15 to 1 ratio (for glycerol, wherein  $n=3$ ) and at least a 15 to 1 ratio.

(e) at page 14, the examiner states:

"Regarding applicants' argument that a preferred ratio of 1:1 is preferred in Barthold et al., applicants fail to recognize that the non-preferable embodiment, Barthold et al. (col. 3, line 50-52) clearly disclose that  $n$  can be as 3, 5 or higher, in view of the explicit teachings of oxyalkylated alcohol prepared from trimethylopropane ( $n=3$ ), pentaerythritol ( $n=5$ ), sorbitol, polyglycerol. Therefore, the examiner has reasonable basis to maintain the rejection set forth."

This again shows a misunderstanding of the claimed invention. The excerpt from the '617 patent relied upon by the examiner discloses no more than the alcohol/polyol than can be reacted with an alkoxide. The excerpt provided by the examiner clearly states that "[E]xamples of suitable alcohols are..." Accordingly, this excerpt merely discloses a large number of alcohol/polymers containing one or more hydroxy groups that can be used, i.e., ethanol ( $n=1$ ) through sorbitol ( $n=6$ ). This disclosure has *nothing* to do *either* with the number of moles used to alkoxylate the alcohol/polyol *or* the number of moles of (meth)acrylic acid used to react with the alkoxylated alcohol/polyol. In contrast to this broad disclosure in the '617 patent, the present claims are not only limited to an polyol wherein  $n=3$ , but are limited to glycerol.

(f) at page 15, the examiner states:

"However, applicants fail to recognize that the examiner fail[sic] to recognize that rationale set forth for the rejection for claims 7, 10 also applied to the rejection of claims 11-13."

In response, applicants are in no position to conjecture that the rationale applied to the rejection of one claim should be extended to another claim that is not addressed in the rejection. It is incumbent upon the examiner to articulate a complete action.

(g) at pages 15-16 of the Office Action, the examiner states:

"Regarding applicants' argument that Barthold et al. fails to teach the molar excess of methacrylic acid in the reaction mixture, applicants fail to recognize that Barthold et al. (col. 3, line 50-52) clearly disclose that  $n$  can be as 3, 5 or higher, in view of the explicit teachings of oxyalkylated alcohol prepared from trimethylpropane ( $n=3$ ), pentaerythritol ( $n=5$ ), sorbitol, polyglycerol, which clearly teach the systematic increase of methacrylic acid as the  $n$  value increases. Therefore, it would have been obvious to one of ordinary skill in art to use an molar excess amount of methacrylic acid as the  $n$  values continues to increase. As for the applicants' argument that Barthold et al. teach away from the molar excess of methacrylic acid, applicants must recognize that the teachings of "polyglyceol" in Barthold (col. 3, line 50-52) clearly indicate that  $n$  is a number that can be optimized through "routine experimentation", motivated by the expectation of success of obtaining the invention of Barthold et al. Since the acid number values are also dependent on the amount methacrylic acid incorporated, the examiner has a reasonable basis to group the rejection of claims 11-12 with 13."

This is a further showing of a misunderstanding of the invention by equating an increasing " $n$ " number with an *excess* molar amount of (meth)acrylic acid. As stated above, the number " $n$ " merely refers to the number of hydroxy groups in the alcohol. As " $n$ " increases, the amount of (meth)acrylic acid can increase in order to react with the greater number of hydroxy groups. This *does* not equate to an *excess* molar amount of (meth)acrylic acid *per* hydroxy group. As discussed above in (e), the '617 patent teaches a molar ratio of methacrylic acid to oxyalkylated alcohol of  $n:1$  to  $1:1$ , i.e., *no* excess, and preferably a deficit, of (meth)acrylic acid per hydroxy group. In contrast, the present claims recite glycerol ( $n=3$ ) and a molar ratio of (meth)acrylic acid to alkoxylated glycerol of at least 3.15 to 1, or at least 15 to 1, i.e., an *excess* of (meth)acrylic acid per the three hydroxy groups of glycerol.

(h) at page 16 of the Office Action, the examiner states:

"Regarding applicants' argument that why would a person skilled in art strip a solvent from a reaction of the entire time of the reaction proceeding, applicants fail to recognize that stripping of a solvent from a reaction in Barthold et al. is unintentional. Rather, the stripping procedure in Barthold et al. is a result of the step of blanketing a reaction. Although the intentions may be different when comparing Barthold et al. when comparing to the invention as claimed, however, the end results are still stripping."

Applicants disagree. The contentions of the examiner are cursory and supported. The '617 patent teaches no more than "under a nitrogen blanket" (column 10, line 54). This cannot be

equated to stripping because the nitrogen blanket can be static and, if not, is a slow stream that is insufficient to remove a solvent. The examiner should further note that the solvent is *not* removed in the example relied upon. At column 11 of the '617 patent it is stated that "the mixture is allowed to cool" (lines 3-4) and that, in the next step, acrylic acid is added "to a solution of the esterified alcohol prepared under A3" (lines 55-56). Accordingly, the "nitrogen atmosphere" is not stripping because the solvent has not been removed. Also, see '617 patent, column 10, line 52 through column 11, line 6 and Example A14 in Table 3. In particular, the reaction began and ended with 268 g of xylene solvent showing that a nitrogen atmosphere blanket did not serve a stripping function.

(i) at page 16 of the Office Action, the examiner further states:

"Regarding applicants' argument that the recited "oxygen-containing gas" means a gas containing O<sub>2</sub> according to the specification (page 22, line 34-35), applicants must recognize that recitation fails to limit oxygen compound to be O<sub>2</sub> gas. Applicants must also recognize that the recitation also include water as an oxygen containing compound."

The examiner misreads the claim, which recites an "oxygen-containing gas". The claim does not recite "an oxygen-containing compound" in the gas, as contended by the examiner. Using an oxygen-containing *compound*, as suggested by the examiner, is an unreasonable extension of the meaning of the term "oxygen-containing gas". Applicants clearly, concisely, and unambiguously recite *oxygen*, i.e., O<sub>2</sub>, as present in the gas. The examiner expands this recitation to mean oxygen as an atom of a constituent in the gas. Such a construction is incorrect in view of the present specification at page 22, lines 34-36. Applicants ask how can molecular oxygen be claimed in any other way than by its basic name, *oxygen*? The meaning of the claim is perfectly clear to persons skilled in the art. Furthermore, an oxygen-containing compound, e.g., water, would not perform the function desired, i.e., inhibition of premature polymerization. Oxygen (O<sub>2</sub>) performs this function; water will not function as an inhibitor of polymerization.

(j) At page 17 of the Office Action, the examiner states:

"Regarding "postcrosslinking", Barthold et al. (col. 7, line 37-50; col. 15, line 41- 54) clearly teach a postcrosslinking process."

This is another example of a misunderstanding of the claimed invention. The excerpt of the '617 patent relied upon by the examiner is *not* directed to postcrosslinking, it is directed to internal crosslinking. Internal crosslinking and surface postcrosslinking are separate processes and achieve different results.

The '617 patent at column 7, lines 37-50, teaches that the molecular weight of the polymers can be increased in a subsequent step by additional crosslinking. As taught by the '617 patent, the polymer prepared therein is in *solution* and an additional crosslinking agent is added to react further with the polymer and increase the molecular weight of the polymer. The result is a viscous solution. See '617 patent, column 15, lines 41-45.

The subsequent postcrosslinking of the '617 patent is different from the postcrosslinking recited in the claims. The present postcrosslinking step is disclosed at page 27, line 33 through page 16. A postcrosslinker is added to crosslink only the surfaces of a hydrogel particle, see specification page 28, lines 2 and 3. A postcrosslinker is applied to the surfaces of the hydrogel particles by spraying, and the resulting particles are heated to dry and surface crosslink the hydrogel.

It is well known in the art to surface postcrosslink SAP particles as set forth in, "Modern Superabsorbent Polymer Technology," F. Buchholz et al., eds., Wiley-VCH, New York, NY (1998), pages 97-103, submitted concurrently with this response as Exhibit C. It is clear that the term "postcrosslinking", as well-known and used in the art of SAPs, refers to surface crosslinking that improves the absorption properties of the SAP. The additional crosslinking is limited to the surface areas of the SAP particles.

This is substantially different from providing additional crosslinks throughout a polymer in solution to increase the molecular weight of the polymer. If the additional crosslinking step of the '617 patent was performed, the resulting particle would not be a *hydrogel*, as claimed. The excessive amount of crosslinking would not permit the absorption

and retention of aqueous fluids required by a hydrogel particle, e.g., an SAP. The additional crosslinking taught in the '617 patent would therefore destroy the hydrogel particles of the present invention.

(k) at page 17 of the Office Action, the examiner further states:

"Regarding "drying", Barthold et al. (col. 8, line 55-61; col. 15, line 55-65) clearly disclose a method of rapid removal of water (drying)."

This is yet another example of a misunderstanding of the invention *and* the cited reference. The relied upon portions of the '617 patent disclose adding "a demulsifier composition" of the '617 patent (i.e., a polymer) to a crude oil emulsion in order to break the emulsion ('617 patent, column 8, lines 49-54). The crude oil emulsions are "easily separated" into clean oil and brine ('617 patent, column 8, lines 40-48). The '617 patent, at line 15, lines 55-65 demonstrates that the *copolymers* demulsify crude oil, and the amount of water "separated off was recorded".

These portions of the '617 patent again relate to the copolymer of an oxyalkylated monomer and a hydrophilic monomer, and *use* of the *polymer* to demulsifying crude oil. These portions of the '617 patent do not remotely relate to the present claims directed to a process for preparing a crosslinked hydrogel particle.

Furthermore, the '617 patent is not remotely directed to the claimed drying step, it is directed to "separating" water from oil in a crude oil emulsion. Present claim 16 recites "drying" the reaction mixture obtained for step k), i.e., removing the remaining water from the hydrogel particles by heating the hydrogel particles. See specification, page 28, lines 1-16.

Importantly, it must be further noted that the drying step recited in the claims refers to drying of the crosslinked hydrogel particles. Should the demulsification of the '617 patent somehow be considered as a drying step, it is the *oil* that is being dried in the '617 patent, not the demulsifying polymer. In contrast to the presently claimed drying step, the polymer of the '617 patent is being *hydrated* by its addition to a water-containing crude oil emulsion.



(l) at page 18 of the Office Action, the examiner reiterates statements relating to blanketing vs. stripping, oxygen-containing gas, and molar excess of methacrylic acid., These statements have been addressed above. In this paragraph the examiner states the following:

"Since Barthold et al. (col. 4, line 67 to col. 5, line 1) clearly indicate that it is not desirable to have gelling occurred[sic], it would not be difficult to one of ordinary skill in art to recognize and to use an excessive amount of methacrylic acid to prevent the gelling caused by the multifunctional alcohol."

This statement is backward. The '617 patent teaches that excess (meth)acrylic acid can cause gelling, not an excess of multifunctional alcohol. See '617 patent, column 4, lines 61 through column 5, line 1. Excess multifunctional alcohol cannot cause gelling. Therefore, the '617 patent teaches that excess methacrylic acid should be avoided, i.e., ratio of multifunctional alcohol:(meth)acrylic acid of "from 1:1 to 1:n" and preferably a ratio of 1:1 (wherein "n" is the number of hydroxy groups in the multifunctional alcohol). In fact, the '617 patent prefers *using* an excess of multifunctional alcohol, i.e., a preferred ratio of 1:1, even for a multifunctional alcohol containing 3 hydroxy groups (n=3), which would leave an average excess of two unreacted hydroxy groups.

(m) at page 18 of the Office Action, the examiner states:

"Regarding applicants' argument to the advisory action of February 12, 2008, applicants argue that the postcrosslinking process of Barthold et al. (col. 15, lines 41- 45) is a viscous solution, applicants must recognize that the claims as written do not exclude a viscous solution."

This statement/argument is incorrect and irrelevant. As discussed above, the '617 patent *does* not teach a postcrosslinking step. A postcrosslinking step requires a solid particle. The '617 patent teaches additional *internal* crosslinking to provide a viscous solution. The additional crosslinking of the '617 patent does not produce a gradient of crosslinking density, but uniform crosslinking throughout the polymer. In fact, the additional crosslinking of the '617 *cannot* produce a crosslinking gradient because the additional crosslinking is not performed on an already crosslinked polymer particle.

(n) at page 18 of the Office Action, the examiner further states:

"Regarding applicants' argument that Barthold et al. is different from the postcrosslinking recited in the claims because the crosslinking as claimed only crosslinke[sic] the surfaces of the hydrogel, applicants must recognize that the claims as written does not restrict the inner part of the hydrogel not to be crosslinked. As long as the surface of the hydrogel has been taught to be crosslinked in Barthold et al., the rejection set forth is proper."

Another example of not understanding the claimed invention. When an ester F containing three (meth)acrylic groups is copolymerized with (meth)acrylic acid, the "inner part of the hydrogel" *must* be crosslinked. This is a result of the multifunctional ester F. The '617 patent does not teach crosslinking only of the surfaces because the polymers are in solution and have no "surfaces".

(o) at page 18, the examiner further states:

"Regarding applicants' argument that the Barthold et al. (col. 8, line 55-61; col. 15, line 55-65) teach a drying step, which involves the copolymer to be demulsify and water "separated off", that is different from the one as claimed, applicants must recognize that the the [sic]argued differences are not supported by the claims as written."

This contention is addressed in (k), above. The drying recited in the claims refers to drying of the hydrogel particles. The '617 patent is directed to adding a copolymer to an emulsion to separate the water from the oil in the emulsion. How such a separation of water from a crude oil emulsifier to form a layer of water and a layer of oil can be equated to drying a hydrogel particle is beyond logic.

(p) finally, at page 18 of the Office Action, the examiner further states:

"Regarding applicants' argument the the [sic] resins of Barthold et al. do not gel, the examiner disagrees because Barthold et al. has (col. 7, line 14) clearly indicated that the disclosed materials have the tendency to gel, it would not be difficult to one of ordinary skill in art to recognize that the disclosed materials can form a gel or hydrogel."

The portion of the '617 patent relied upon by the examiner is not directed to the copolymers of the reference, but to neutralizing the remaining catalytic amounts of acid in the reaction mixture. By neutralizing the acid, no further reaction occurs and gelling is prevented.

All pending claims are in a form and scope for allowance. An early and favorable action on the merits is respectfully requested.

Should the examiner wish to discuss the foregoing, or any matter of form in an effort to advance this application toward allowance, the examiner is urged to telephone the undersigned at the indicated number.

Dated: June 8, 2009

Respectfully submitted,

By 

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# MODERN SUPERABSORBENT POLYMER TECHNOLOGY

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**Preface**

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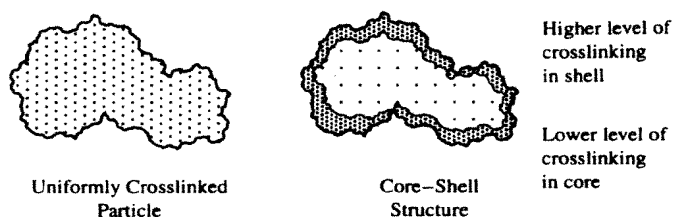
2.2.2.

### 3.2.8. Addition of Post-Treatments

**3.2.8.1. Advanced Products.** The processes described above produce a particle with crosslinking that may be assumed to be essentially uniform throughout the particle. As such, the swelling and modulus behavior of the product particles can be described by theories of network swelling and elasticity (see Chapter 5). One problem associated with these superabsorbent polymers was also recognized in a variety of water soluble polymers, e.g., poly(acrylamide), cellulose ethers,<sup>95</sup> or soluble poly(acrylic acid).<sup>96</sup> This problem is the tendency of the granular polymers to clump, "gel block," or form fish-eyes when aqueous liquids are added to them or they are added to aqueous liquids. The surfaces of the massed particles swell rapidly to form a soft, deformable layer. The resulting particle deformation and interparticle adhesion reduces interparticle porosity and limits the swelling rate of the polymer mass to the diffusion rate of liquid through the partially swollen mass.

The first attempts to solve this problem in highly absorbent anionic polyelectrolytes used multivalent cations to form a crosslinked surface layer that was more rigid than the original core polymer.<sup>97</sup> Subsequently, to give products with improved dispersibility and absorption rate, the surface of crosslinked polyacrylate particles was reacted with a variety of multifunctional organic compounds.<sup>49,50,98,99</sup> This structural improvement is shown schematically in Figure 3.9. Swelling capacity data as a function of particle size readily demonstrate that a shell of real, as opposed to infinitesimal, thickness is formed by surface crosslinking processes. The shell of higher crosslink density provides a more rigid surface layer during swelling and prevents the gel-blocking that would otherwise occur early in the swelling process (Chapter 5). As a result, liquid can flow through the bed of particles to each particle, increasing the effective surface area available for swelling and the apparent swelling rate. The swelling and modulus behavior of structured particles are discussed in Chapter 5.

Because a surface layer is formed on each individual particle, the crosslinking reaction, but not necessarily the reagent addition, must occur after achieving the desired particle size distribution. Any compound that can react with two or more functional groups on the polymer backbone can function as a surface crosslinking reagent. For superabsorbents, this requires reagents that can react with the car-



**Figure 3.9.** Schematic representation of a uniformly crosslinked superabsorbent particle and a structured particle with a surface layer of higher crosslink density.

boxylic acid or carboxylate moieties on separate, adjacent polymer chains. Quaternary amines have been used,<sup>100</sup> but the most common reagents add surface crosslink density as a result of formation of ester crosslinks. These surface crosslinking agents include polyhydric alcohols,<sup>49,50</sup> glycidyl compounds,<sup>101-103</sup> and alkylene carbonates.<sup>104</sup>

Blenders suitable for the addition of surface crosslinking agents include screw mixers, ribbon mixers, fluidized beds,<sup>49</sup> high-speed rotating paddle mixers,<sup>50,90</sup> vortex mixers, rolling mixers, or double screw mixers.<sup>104</sup> Spraying the surface crosslinking reagent into the blender, using small droplet sizes, preferably less than 300  $\mu\text{m}$ , helps reduce the amount of liquid required to disperse the surface crosslinking reagent.<sup>50</sup> A high-speed paddle mixer used for this process operates at greater than about 600 m/min of a lead-end peripheral speed.<sup>90</sup> In one example, a Turbulizer, produced by Hoskawa Micron K. K., was operated at 3,000 rpm. The inner surface of the mixer is preferably coated with a material that minimizes adhesion of the wetted polymer to the walls of the mixer, for example, polypropylene or a poly(tetrafluoroethylene) resin. When a high-speed mixer is used, the amount of organic solvent used to help disperse the surface crosslinking reagent may be minimized or even completely eliminated.

A heating step is normally necessary for the reaction of surface crosslinking agents with the partially neutralized poly(acrylic acid) backbone. The time and temperature of heat treatment are chosen, considering the reactivity of the crosslinking reagent, to give the desired end-use properties. Naturally, longer reaction times and higher temperatures increase, for a reagent of any reactivity, the extent of reaction. Tsubakimoto et al.,<sup>50</sup> claim temperatures of 90°–300°C while Dahmen and Mertens<sup>104</sup> teach 150°–300°C. However, at temperatures greater than about 250°C, degradation of the polyacrylate by oxidation or decarboxylation may become significant (see Chapter 2, Section 2.5.4.2). More specifically, the reactive epoxy groups in ethylene glycol diglycidyl ether react in 30 min at 140°C.<sup>105</sup> The less reactive ethylene carbonate requires 1 h at 180°C or 15 min at 215°C.<sup>104</sup>

Suitable heating devices include fluidized-bed dryers, infrared dryers, agitated-trough dryers,<sup>49</sup> paddle dryers,<sup>50</sup> vortex dryers, or rotating-disc dryers.<sup>104</sup> Comparative data that would allow the selection of the most suitable device are not given. Both direct-contact dryers (rotating-disc dryers, paddle dryers) and fluidized-bed dryers are used commercially to provide heat for the reaction step. Direct-contact dryers deliver heat to the polymer particles by contact of the particles with a hot surface, while fluidized-bed dryers deliver heat to the particles with a stream of hot air of high enough velocity to suspend the particles in the airstream. Direct-contact dryers, for this application, must be designed keeping in mind the possibility of attrition of the particle surface (from the mechanical action of the paddles or other movable surfaces on the particles) and consequent degradation in product properties. The air-handling equipment associated with fluidized-bed dryers may make them expensive to operate.

Initially, structured particle technology was viewed as solving the problem of gel-blocking, as measured by a fish-eye test<sup>49</sup> or a similar test conducted without a compressive load. These early tests were only able to qualitatively distinguish be-

tween structures. For example, Tsubaki crosslinking reagents (when the reagent load) were able to deliver different sections of the reagent over the surface, resulting in different success in the process.

Optimization of sorbency under crosslinking reagents as alcohol or acetone with these appropriate temperatures for surface crosslinking in water cause the structure to collapse, such as the structure of the treatment. The reagents with the process.<sup>50,90</sup> The agents over the process or prevent agglomeration. The use of recovery and recycling require extra equipment.

Adding 0.2 v neutralized polyacrylate of reagent powder. Twenty-five dish for 15 min plate as a heat treatment. Chapter 4, section 4.6.4.2) data solution increase ethyleneglycol crosslinking reagent. This has reagent into the structure than just on the surface.

Other processes for glycerol the on the values of may be reduced. Increasing the s-

polymer chains. Quaternary salts add surface crosslinking agents, surface crosslinking agents,<sup>101-103</sup> and alkylene

g agents include screw paddle mixers,<sup>50,90</sup> vortex mixers, and spray nozzles. Spraying the surface crosslinking agent is preferred, preferably less than 100 psi, to disperse the surface crosslinking agent. This process operates at 3,000 rpm. The initial speed is 3,000 rpm. The initial speed that minimizes adhesion is 3,000 rpm. For example, polypropylene or polyethylene is used, the amount of crosslinking reagent may be mini-

of surface crosslinking agent. The time and temperature of the crosslinking reaction times and the extent of reaction. While Dahmen and Dahmen<sup>90</sup> used water at about 250°C, the reaction may become significant for reactive epoxy groups.<sup>95</sup> The less reactive eth-

frated dryers, agitated-dryers, fluidized-bed dryers,<sup>104</sup> Comparison of these devices are not given. Direct-contact dryers and fluidized-bed dryers are not given. Direct-contact dryers with a hot surface and a stream of hot air are not given. Direct-contact dryers with a hot surface and a stream of hot air are not given. Direct-contact dryers with a hot surface and a stream of hot air are not given.

solving the problem of direct contact drying without a stream of hot air. Directly distinguishing be-

tween structured polymers made under different sets of process conditions. For example, Tsubakimoto et al.<sup>50</sup> showed that a water/alcohol carrier for the surface crosslinking reagent yields a structured polymer with less fish-eye formation than when the reagent is added undiluted. Later, more sophisticated tests (see Chapter 4, section 4.6.4) that measure swelling under a compressive load (absorbency under load) were able to quantitatively distinguish between structured polymers made under different sets of process conditions. Results of these tests suggest that penetration of the reagent into the particles and control of the dispersion of the crosslinking agent over the surface of the particles are critical process considerations for achieving success in the absorbency under load test.

Optimization of the surface crosslinking process to reduce gel-blocking in an absorbency under load test has been addressed in a number of ways. Surface crosslinking reagents have been added in aqueous solutions and other diluents such as alcohol or aqueous salt solutions.<sup>102,103</sup> However, there are several difficulties with these approaches.<sup>106</sup> Water swells the particle surface and lowers the glass transition temperature of the polymer at the surface, increasing penetration of the surface crosslinking agent into the polymer particle. However, excessive amounts of water cause the polymer to swell and can make handling difficult. Inorganic particulates, such as silicates, in addition to controlling the hydrophilic/hydrophobic balance of the treatment reagent, are used, in combination with high-speed blending of the reagents with the polymer, to control agglomeration during the reagent addition process.<sup>50,90</sup> The alcohol or salt solution helps disperse the surface crosslinking agents over the powder by diluting the crosslinker (larger volume) and helps control or prevent agglomeration of the powder by reducing the activity of water in the solution. The use of an organic solvent has the obvious disadvantage of requiring recovery and recycle. Also, for example with the lower alcohols, the low flash points require extra equipment and more safeguards to maintain safe operation.

Adding 0.2 wt% glycerol, in combinations of water and *n*-propanol, to a 65% neutralized polyacrylate made by the process of Siddall and Johnson<sup>28</sup> shows the effect of reagent penetration. One gram of liquid was added to 100 g of polymer powder. Twenty-five grams of the reagent treated polymers was heated in an aluminum dish for 15 min at 200°C in a preheated circulating-air oven equipped with a steel plate as a heat sink. Table 3.5 shows the swelling capacity (method described in Chapter 4, section 4.6.1.2) and absorbency under load (described in Chapter 4, section 4.6.4.2) data. Swelling capacity decreases as the amount of water in the reagent solution increases. Similar results have been obtained by using aluminum acetate, ethyleneglycol diglycidyl ether, or ethylene carbonate as the surface crosslinking reagent. This has been interpreted as resulting from increased penetration of the reagent into the particle and increased crosslinking throughout the particle rather than just on the surface.

Other process choices also affect the resulting properties. Table 3.5 suggests that for glycerol the optimum weight ratio of water to *n*-propanol is about 30:70 (based on the values of swelling capacity and absorbency under load). The amount of water may be reduced by choosing a more hydrophilic organic solvent such as methanol. Increasing the salt concentration of the crosslinker solution also decreases the hy-



**Table 3.5. The effect of solvent hydrophilicity on the properties resulting from surface crosslinking of a polyacrylate treated with 0.2 wt% glycerol and then heated at 200°C for 15 min**

Solvent Composition Water/ <i>n</i> -propanol (w/w)	Swelling Capacity (g/g)	Absorbency Under 2.0 kPa Load (g/g)
Starting material	39.0	9.0
0/100	36.4	23.2
10/90	35.0	21.6
20/80	34.7	29.0
30/70	28.8	29.3
40/60	30.5	29.3
50/50	29.3	28.6

drophilicity of the solution (reduced particle surface swelling) and has the expected effect on product quality. The amount of crosslinker solution and the concentration of crosslinker in the solution also impact the results. When too little crosslinker solution is used, for example to avoid agglomeration, the particle surface coverage can be incomplete, leading to increased gel-blocking in the swelling under load tests. When the concentration of crosslinker is too low, or an insufficient quantity of reagent is applied, the amount of additional crosslinking at the surface does not make the surface sufficiently rigid to give the required resistance to gel-blocking.

More recently, the desire for products with an improved combination of swelling capacity and absorption under load<sup>107,108</sup> has led to more complex surface crosslinking systems.<sup>100,106,109</sup> In one case,<sup>100</sup> a shell structure is achieved by using two surface crosslinking reagents with different solubility parameters, one greater than 12.5 (cal/g<sup>3</sup>)<sup>1/2</sup> and the other less than 12.5 (cal/g<sup>3</sup>)<sup>1/2</sup>. The combination of solubility parameter and low molecular weight of the crosslinking reagents (less than 350 g/mol) is said to optimize the penetration of the surface crosslinking reagent into the particle (compare row 4 to rows 2 and 3 of Table 3.6). In a second case, surface crosslinking with a specific class of high-molecular-weight (greater than 1,000 g/mol) azetidinium compounds leads to polymer particles with more ideal shell thicknesses (less than 10% of the particle radius).<sup>109</sup> The high molecular weight of the reagent limits the penetration of the crosslinking agent into the particle so that the swelling capacity is not reduced too greatly. A range of surface tension, about 40–50 dynes/cm, of the applied crosslinker solution promotes spreading of the crosslinker solution over the surface of the particles.<sup>110</sup> A two-step addition of surface crosslinking agent also leads to improved properties.<sup>111</sup> Another two-part process, in which a first crosslinker (hydrophilic polymer or metallic compound) is reacted with a second additive on the surface of a wet polymer (10–100 parts), has also been described. The extent of hydration of the polymer and crosslinker are chosen to give the desired penetration of the surface crosslinking reagents into the particle and the desired combination of properties. The process seems most suitable for suspension-made polymers, but its inventors claim its utility is for polymers made by solution polymerization. In one example, a coating of poly(ethyleneimine)

**Table 3.6. A crosslinking structure**

Reagent
Aluminum acetate
Glycerol
EGDGE <sup>a</sup>
Glycerol/EGDGE <sup>a</sup>
(process of I et al. <sup>109</sup> )
Ethylene carbonate
Example 1 of E and Hartan <sup>11</sup>
Process of Burg et al. <sup>112</sup>

<sup>a</sup>Ethylene glycol  
<sup>b</sup>Method of Chap  
<sup>c</sup>Method of Chap

crosslinked with  
resin with "ex  
This process is  
reaction.

Despite the  
swelling differ  
be produced  
swelling cap  
crosslinking r  
neutralized po  
chosen to give  
capacity (35 g/g  
on data in the

The surface  
tured particle  
produce simila  
under load wa  
crosslinking. I  
surface crossl  
process. Some  
conditions, su  
2, section 2.7.  
tion that the c  
structured part  
be such a facto

ulting from surface  
on heated at 200°C

Absorbency Under 0 kPa Load (g/g)
9.0
23.2
21.6
29.0
29.3
29.3
28.6

and has the expected  
and the concentration  
little crosslinker so-  
surface coverage can  
ng under load tests.  
fficient quantity of  
ie surface does not  
e to gel-blocking.  
bination of swelling  
e complex surface  
s achieved by using  
imeters, one greater  
combination of sol-  
reagents (less than  
crosslinking reagent  
a second case, sur-  
(greater than 1,000  
th more ideal shell  
molecular weight of  
the particle so that  
face tension, about  
s spreading of the  
step addition of sur-  
Another two-part  
tallic compound) is  
(10-100 parts), has  
crosslinker are cho-  
agents into the par-  
ns most suitable for  
for polymers made  
poly(ethyleneimine)

**Table 3.6. A comparison of properties resulting from "optimum" process conditions for making structured particles**

Reagent	Swelling Capacity <sup>b</sup>		Absorbency Under Load <sup>c</sup> (g/g)		
	Before Treatment (g/g)	Swelling Capacity (g/g)	2.0 kPa	3.9 kPa	6.2 kPa
Aluminum acetate	39	35	25	18	—
Glycerol	39	35	33	21	12
EGDGE <sup>a</sup>	40	35	35	31	24
Glycerol/EGDGE (process of Date et al. <sup>109</sup> )	45	35	35	31	26
Ethylene carbonate	50	36	30	25	21
Example 1 of Brehm and Hartan <sup>111</sup>	40	36	33	25	21
Process of Burgert et al. <sup>112</sup>	39	36	32	26	22

<sup>a</sup>Ethyleneglycol diglycidyl ether.

<sup>b</sup>Method of Chapter 4 Section 4.6.1.2.

<sup>c</sup>Method of Chapter 4 Section 4.6.4.2.

crosslinked with a polyglycerol polyglycidyl ether resulted in a superabsorbent resin with "excellent" stability (by which the inventors seem to mean gel modulus). This process is said to require less stringent temperature control to achieve adequate reaction.

Despite the differences in the various surface crosslinking reagents and the resulting differences in reaction conditions, products with very similar properties may be produced with a variety of surface crosslinking processes. Table 3.6 shows swelling capacity and absorbency under load results when a variety of surface crosslinking reagents were applied in a methanol/water solvent system to a 65% neutralized poly(acrylic acid). The reaction conditions (temperature and time) were chosen to give the highest values of absorbency under load at the target swelling capacity (35 g/g). The choices were based on our experience with these processes and on data in the indicated references.

The surface crosslinking process of Brehm and Hartan<sup>111</sup> and the alternate structured particle technology of Burgert et al.<sup>112</sup> (discussed in more detail below) also produce similar results (last two rows of Table 3.6). In each case, the absorbency under load was substantially improved compared with the material before surface crosslinking. Even so, property differences remain that depend on the individual surface crosslinking reagents or process, despite our attempts to optimize the process. Some of these may result from insufficient optimization of the process conditions, such as spreading of the reagent, or chemistry, as discussed in Chapter 2, section 2.7. However, a consideration of the several reagents leads to the speculation that the crosslinker structure might also be a factor in the performance of the structured particle. The distance between functional groups in the crosslinker might be such a factor. This is a question that needs to be resolved by future study.

Improved properties have also been achieved by forming a structured particle in a different way. Polymers made with certain crosslinkers or combinations of crosslinkers and heated in the presence of special oxidizing agents have dramatically improved absorbency under load and swelling capacity.<sup>112</sup> In this technology, all necessary ingredients are added prior to polymerization so that they are mixed uniformly in the resulting particles. A variety of primary crosslinkers may be used alone or in combination with a secondary crosslinker, also uniformly distributed throughout the particle. Primary crosslinkers that have been used include 1,1,1-trimethylolpropane triacrylate (TMPTA), ethoxylated TMPTA, allyl methacrylate, and various diacrylates and methacrylates based on poly(ethyleneglycol). Nonvinyl or bimodal secondary crosslinkers have been used. Examples of nonvinyl crosslinkers include glycerol, various molecular weight poly(ethyleneglycols), and ethyleneglycol diglycidyl ether. Bimodal crosslinkers include hydroxyethyl acrylate and acrylate or methacrylate esters of polyethylene glycols. The preferred oxidizing agent is sodium or potassium chlorate. The amount of chlorate affects the reduction in the level of unreacted monomer, the amount of extractable polymer in the product, and the final swelling capacity. Figure 3.10 is a graph of data from examples 78–86 of Burgert et al.,<sup>112</sup> in which polymer samples were heated for 20 min after reaching 200°C. As the level of chlorate increases, swelling capacity and extractable polymer increase. The optimum chlorate level, considering swelling capacity, extractable polymer, absorbency under load, and unreacted monomer, is about 200 ppm. The moisture remaining in the particle, after drying and grinding and prior to the reaction step, influences the magnitude of the observed oxidizer effect.

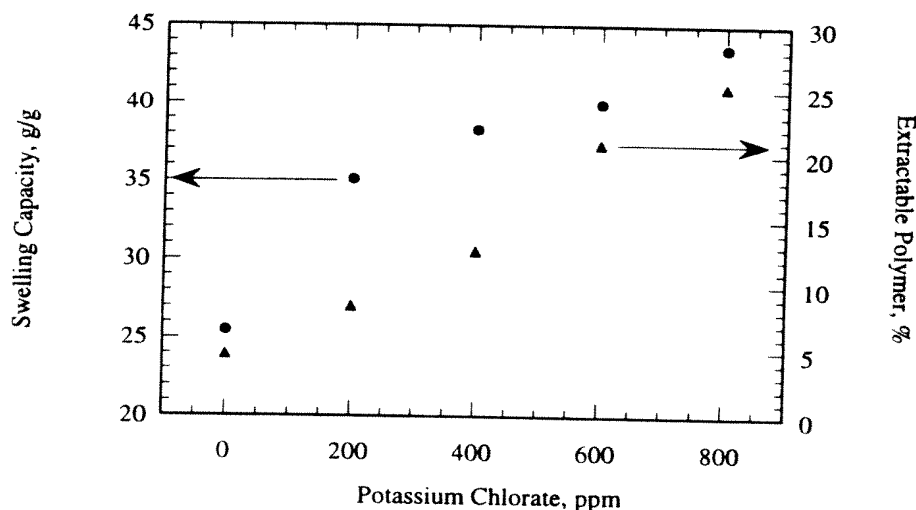


Figure 3.10. The effect of chlorate level on the swelling capacity (●) and extractable polymer (▲) of structured particle product made by the process of Burgert et al.<sup>112</sup>

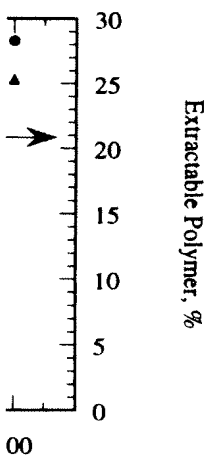
The reaction time should be 10–30 min when the heating is complete, and absorbency under load, even under nearly equivalent conditions, is substantially because of the reaction time.

A consequence of degradation of the particle surface fraction means of prevention of the addition of about 10% of the superabsorbent polymer" also refers to the particle surface.

**3.2.8.2. Additives.** The final product in crosslinking, as crosslinking additives.<sup>115</sup> Both (less than 10 μm) other or to larger typically blended active additive to face crosslinking.

Additives that improve polymer scope of this process in humid air. In a manner as required in practice or eliminate. However, particularly available in inadequate dry flow materials for use with copolymers of acrylate polyalkylene glycol (amide).<sup>118</sup> Quaternary alone or in combination with the silica anti-caking types of commercial

actured particle in combinations of s have dramatical- his technology, all ey are mixed uni- kers may be used or- mly distributed ed include 1,1,1- llyl methacrylate, glycol). Nonvinyl onvinyl crosslink- ycols), and ethyl- ethyl acrylate and eferred oxidizing ects the reduction ymer in the prod- ta from examples d for 20 min after ity and extractable lling capacity, ex- ner, is about 200 nding and prior to er effect.



d extractable polymer

The reaction temperature should be between 170° and 235°C, and the heating time should be less than 40 min. The best combination of product properties occurs when the heating temperature is between 210°–230°C. Heating times at 230°C of 10–30 min yielded product with nearly the same swelling capacity, extractable polymer, and absorbency under load. Combinations of swelling capacity and absorbency under load, even at high imposed loads, made by this technology (Tables 3.6) are nearly equivalent to properties achieved with surface crosslinking technology, presumably because gel-blocking is limited by a surface layer of higher crosslink density.

A consequence of the “core-shell” particle structure (Fig. 3.9) is a vulnerability to degradation of product quality by fracture of the particle surface.<sup>82</sup> High-quality methods for handling the solid product are required (see section 3.2.6) to avoid particle surface fracture and consequent degradation of product properties. Chemical means of preventing surface degradation have also been disclosed. For example, the addition of about 10 mol% of a monomer such as poly(ethylene glycol) acrylate improves the fracture resistance of the resulting superabsorbent product.<sup>113</sup> Coating the superabsorbent particles with a “non-reactive, water-insoluble, film-forming polymer” also reduces the dust level (small particle size fraction from abrasion of the particle surface in a ball mill test).<sup>114</sup>

**3.2.8.2. Additives for Improved Handling.** Techniques to reduce dust in the final product include agglomeration of the finer dusty particles via surface crosslinking, as described above, or the addition of low levels of hydrophilic liquid additives.<sup>115</sup> Both techniques reduce the concentration of air-borne respirable dust (less than 10  $\mu\text{m}$  in diameter) by agglomerating the fine particles either to one another or to larger particles. When low levels of liquid additives are used, they are typically blended into the final product just prior to packaging. In one case, a nonreactive additive to reduce product dustiness may be added concurrently with any surface crosslinking reagents.<sup>110</sup>

Additives that reduce the rate of moisture absorption in humid environments and improve polymer flow characteristics are also of interest. One can appreciate the scope of this problem by simply exposing a quantity of superabsorbent polymer to humid air. In a matter of a few hours, the polymer begins to clump and will not flow as required in processing in a diaper plant. Dehumidified air may be used to alleviate or eliminate this problem, either in polymer or end-use manufacturing plants. However, particularly in the tropical Pacific markets, dehumidified air is not commonly available in diaper manufacturing plants, and additives must be used to allow adequate dry flow of the polymer. A number of such additives are known: oily materials for use with hygroscopic fertilizers,<sup>116</sup> polymeric soaps as drying aids for copolymers of acrylamide,<sup>117</sup> and particulate silica in combination with polyols or polyalkylene glycols as a flow aid for polymers and copolymers of poly(acrylamide).<sup>118</sup> Quaternary surfactants have also been found useful as anti-clump aids, alone or in combination with additives, to reduce product dustiness (a drawback of the silica anti-caking technology).<sup>119</sup> These chemicals may be added in a variety of types of commercial blenders.